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(54) **Ion selective electrode and method of manufacture**

Ionenselektive Elektrode und Verfahren zur Herstellung derselben

Electrode sélective aux ions et procédé pour sa fabrication

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(56) References cited:
EP-A- 0 024 192 EP-A- 0 168 666
GB-A- 2 102 963 US-A- 4 214 968
US-A- 4 337 279

- **THIN SOLID FILMS. vol. 181, no. 1, 10 December 1989, LAUSANNE CH pages 451 - 460 V.ANDRE ET AL 'in-situ metallization of polypropylene films pretreated in a nitrogen or ammonia low-pressure plasma'**
- **DATABASE WPIL Week 9007, Derwent Publications Ltd., London, GB; AN 90-047593**

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Description

The present invention relates to a method of producing an ion selective electrode, in particular ion selective electrodes having Ag/Ni deposited films.

Ion selective electrodes (ISE) are used in the medical field, for example as blood analyzer assays. The particular ISE which the present invention is primarily concerned with is a multi-layer ISE having vacuum deposited Ag/Ni coatings deposited on a plastic substrate. U.S. Patent No. 4,214,968 and EP 24192 disclose such ISE's and methods for their manufacture. A particular preferred substrate for the present invention is polyethylene terephthalate (PET).

Prior to the process of the present invention, the method of manufacturing Ag/Ni electrodes consisted of first providing a PET substrate with an adhesion promoting sub-coating thereon, such as poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid), to improve the adhesion between the PET substrate and the deposited metal layers. A silver layer was then vacuum deposited over the sub-coating. Prior to the subsequent step of depositing nickel, the silver layer required aging of approximately 10 weeks. After the aging process, nickel was selectively deposited in a striped formation over the silver layer. The exposed silver areas were then exposed to a bleaching agent which converted a portion of the silver layer to AgCl. If the silver was not aged sufficiently prior to the Ni deposition step, then during the bleaching operation cracking would frequently occur in the silver layer between the nickel stripes, rendering the electrode useless. The mechanism which caused the cracking is unknown. Since the cracking occurred regardless of whether the adhesion promoting sublayer was employed and in fact occurred even on electrodes that exhibited relatively good PET/Ag adhesion, the cracking did not seem to be adhesion related. Consequently, prior to the nickel deposition, to achieve the requisite aging, the silver deposited on the PET substrate required storage for some 10 to 12 weeks, greatly increasing manufacturing cost. Further, prior to the present invention, an adhesion promoting sublayer, mentioned above, was needed to prevent both cracking and delamination of the electrode during manufacture.

Glow discharge pretreatment and similar techniques are known techniques for improving the adhesion between polymer substrates and metal coatings deposited by physical deposition processes. In glow discharge techniques, a brush or glow discharge is created by introducing residual gasses into a vacuum chamber and applying a high voltage in order to create ions which activate the polymer substrate surface. Examples of the gasses which can be introduced into the vacuum chamber include air, oxygen, nitrogen, helium, neon, argon, krypton, xenon, and radon. After the glow discharge activation, the metal film is deposited by techniques such as electroless plating, evaporation, and sputtering.

The problem is that the prior art does not teach a

method for producing Ag/Ni ion selective electrodes which does not require long aging periods for the Ag layer prior to the Ni deposition and bleaching operation.

The present invention overcomes the above problem by providing a method for applying metal coating according to claim 1.

The method of the present invention may be used to produce electrochemical analysis elements, such as ion selective electrodes, according to claim 2. In the method the conductive metal deposition and bleaching steps may be performed immediately after silver deposition. Optimally, a portion of the uncoated areas of the silver may be coated with various ion transport facilitating gel compositions, or a protective material, such as cellulose acetate.

The method of claim 2 provides an ion selection electrode according claim 7.

Figure 1 illustrates a Ag/Ni ion selective electrode produced in accordance with the present invention.

Figure 2 schematically illustrates an apparatus for carrying out the method of the present invention.

In accordance with the method of the present invention, it has been discovered that, by pretreating a PET substrate by glow discharge in a nitrogen containing atmosphere, silver and nickel coatings may be deposited in immediate successive deposition operations, without the need for substantial aging of the silver layer prior to deposition of the nickel layer. The composite structure may then be immediately bleached to convert a portion of the silver to a silver halide. By using a low energy glow discharge in a nitrogen containing atmosphere to treat the organic substrate the surface chemistry of the substrate is altered to include nitrogen in its structure. In distinction from many ion beam energy techniques of the prior art, the present invention requires the presence of nitrogen in the glow discharge atmosphere.

The preferred ion selective electrode (ISE) of the present invention consists of a polymeric substrate, to which is directly deposited a layer of Ag. A layer of nickel is selectively deposited over the silver layer. The composite structure is then bleached to convert a portion of the silver layer to a silver halide, such as AgCl. Thus, the ISE of the present invention utilizes no adhesion promoting sublayer. Alternatively, the AgCl maybe covered with gels and a protective or ion selective membrane.

The substrates are organic materials including plastics, polyimide, polyesters, Mylar™ (a trademark of E.I. duPont DeNemours), epoxies, and so forth. Typically, the substrates are organic polymers. A preferred substrate is poly(ethylene terephthalate) (PET).

Substrate treatment and metal deposition can occur over a range of temperatures, including room temperature and elevated temperatures. Commercially available apparatus can be used to provide the glow discharge pretreatment as well as the metal deposition steps, which are preferably dry processing steps, in particular e-beam evaporation. In contrast with prior manufacturing operations, no adhesion promoting layer is applied

prior to silver deposition, and yet increased performance of the resultant multi-layer film is exhibited even over those films that were deposited using adhesion promoting sublayers. In particular, there is no evidence of cracking of the silver layer during the bleaching operation, even though the operation may be conducted within days, and preferably immediately after silver deposition. This is particularly significant because prior to the method of the present invention, the cracking problem was only avoidable by aging the silver layer for approximately 10 weeks.

A silver/nickel ion selective electrode produced in accordance with the present invention is illustrated in Figure 1. The electrode 1 typically includes a PET substrate 2, which, after being treated by a nitrogen glow discharge, has a coating of silver 4 deposited thereon. Prior art devices usually utilize an adhesion promoting sub-layer between the silver and the PET substrate. However, because of the nitrogen glow discharge pretreatment there is no need for an adhesion promoting layer in the present invention. A series of nickel stripes 6 is selectively deposited over the silver layer 4, after which the entire operation is exposed to a bleaching solution which converts a portion 8 of the silver layer 4 to silver chloride. The apparatus of this point is operable as a chloride ion sensitive electrode. Alternatively, various electrolyte containing gels 10 and ion selective membranes 11 may be selectively applied over the silver chloride portion 8 to make the ISE sensitive to various other ions. For an explanation of examples of such gels and membranes, see U.S. Patent No. 4,214,968.

An apparatus 20 suitable for carrying out the method of the present invention to manufacture ISEs is illustrated in Figure 2. The apparatus 20 as illustrated is a single in-line vacuum web coating apparatus. Consequently, the apparatus 20 has a glow discharge sub-chamber 22, a silver deposition chamber 24 having a silver source crucible 25, and a nickel deposition chamber 26 having a nickel source crucible 27. Of course, more deposition chambers could be utilized if desired. Alternatively, both chamber 24 and 26 could be used to deposit first Ag, after which crucibles 25 and 27 could be changed to deposit nickel. A vacuum pump 28 is connected to the apparatus 20 to achieve a suitable pressure, preferably below 7×10^{-3} Pascals. Glow discharge chamber 20 is similar to many conventional sputtering subchambers, and includes a conventional cathode 30, and is supplied with a nitrogen containing atmosphere via gas inlet 31. Cathode 30 is preferably made of a material having a low sputtering coefficient to prevent sputtering of the cathode material onto the plastic substrate during the glow discharge pretreatment. Examples of materials having a low sputtering coefficient include aluminum and stainless steel.

A substrate material 32, which is stored on input roller 34, is fed first into the glow discharge chamber 22, where it receives a glow discharge treatment in the presence of nitrogen, as discussed above. Subsequent anal-

ysis of the substrate by X-ray photoelectron spectroscopy (XPS) indicates that such a plasma treatment results in nitrogen being chemically incorporated into the surface structure of the substrate at specific sites. In the case of PET, the nitrogen typically reacts with organic materials in the PET to form nitrogen amines, imines and amides. The substrate is then transported to the coating chambers 24 and 26, where the Ag and Ni layers are applied, after which the substrate is wound onto output roller 43. The silver and nickel deposition chambers 24 and 26 are similar to conventional e-beam evaporation apparatus, and include, for example, a conventional e-beam gun and crucible which holds the metal to be deposited.

A water cooled mask 44 is provided in the nickel deposition chamber 26 to mask areas of the PET substrate 29 when desired, so that, for example, the nickel can be selectively applied in a striped configuration as described above.

The principle of plasma treatment will be briefly described. When an electric field is applied to a gas kept at a reduced pressure, free electrons which are present in a minor proportion in the gas and have a remarkably greater inter-molecular distance than under atmospheric pressure are accelerated under the electric field to gain a kinetic energy (electron temperature). These accelerated electrons collide against atoms and molecules to fracture their atomic and molecular orbitals to thereby dissociate them into normally unstable chemical species such as electrons, ions, neutral radicals, and so forth. The dissociated electrons are again accelerated under the electric field to dissociate further atoms and molecules. The chain reaction causes any gases present to be instantaneously converted into a highly ionized state. This is generally called a plasma. Since gaseous molecules have less chance of collision with electrons and absorb little energy, they are kept at a temperature approximate to room temperature. Such a system in which the kinetic energy (electron temperature) of electrons and the thermal motion (gas temperature) of molecules are not correlated is designated as a low temperature plasma.

Glow discharge pretreatment of prior art devices usually involve oxygen, commonly up to 100%, as the active component of the atmosphere during glow discharge. However, atmospheres containing oxygen are not preferred for the method of the present invention. The preferred glow discharge atmosphere of the present invention is one containing nitrogen. The remainder of the atmosphere may consist of an inert gas. A preferred inert gas is argon. Thus, for example, a suitable atmosphere for carrying out the glow discharge pretreatment step in accordance with the present invention is an atmosphere of 98% argon and 2% nitrogen.

Because nitrogen is incorporated into the polymer surface, covalent bonding can occur between the silver coating and the modified polymer structure. It is believed that this phenomena is responsible for the increased ad-

hesion of the silver layer inherent with the ISEs of the present invention. More importantly, however, when prepared using the glow discharge pretreatment described herein, the silver layer exhibits no cracking during the bleaching operation of the manufacturing process.

It should be noted that adhesion of Ag to the PET layer after glow discharge treatment does fall off with time. For example, there is a noticeable decrease in adhesion if a waiting period of 10 hours or more occurs prior to silver coating deposition. Therefore, ideally the manufacture of the ion selective electrode of the present invention should take place in successive steps, preferably within the same apparatus. However, this is not essential to the practice of the invention, and thus the invention can be carried out in separate apparatus and also with or without a short waiting period prior to nickel deposition.

The beneficial effect of nitrogen glow discharge is dependent upon system parameters, which include, for example, the geometry of the chamber, nitrogen content and pressure in the chamber, and cathode power. Another important variable is treatment energy E , which is equal to the power applied to the cathode (in watts) \times exposure time divided by cathode area. For a given glow discharge chamber, below a certain threshold treatment energy, the nitrogen glow discharge will not alleviate the cracking phenomena. On the other hand, above a certain treatment energy, damage will occur to the substrate.

For the particular glow discharge apparatus described herein, which is a parallel plate chamber (cathode is parallel to the substrate surface) having a cathode to substrate distance of 12.7 cm and a cathode area of 329 cm², vacuum base pressure during glow discharge pretreatment is preferably maintained at the 7×10^{-3} Pascals range or lower. More preferably, the base pressure is maintained below 1×10^{-3} Pascals. During the glow discharge treatment, pressure in the glow discharge chamber is typically 1 to 67 Pascals, and preferably 6.7 to 14 Pascals. The voltage applied to create the glow discharge plasma when such pressures are used is in the range of 700 to 1200 volts. The voltage applied is relatively low in order to avoid deposition of the cathode material, which is purposefully chosen to have a low sputtering coefficient for the same reason. These parameters result in a treatment energy between 1.1 and 4 joules/cm².

After glow discharge pretreatment of the PET substrate, a 600 to 800 nanometer thick film of silver metal is deposited on the PET substrate in deposition chamber 24. A preferred method for deposition of the silver layer is e-beam evaporation. Electron beam vacuum evaporation is a standard deposition technique wherein vapors are produced from material located in a source (usually a crucible filled with the material to be deposited) which is heated by direct impingement by a stream of electrons from an electron beam gun. For example,

see Maissel & Glang, Handbook of Thin Film Technology, Part 1, Section 21, pp 53-54. The silver metal then vaporizes, and rises upwardly, where it deposits on the PET substrate. The process is usually carried out in vacuum (typically 10^{-2} to 10^{-3} Pascals) so the evaporated atoms undergo an essentially collision-less line of sight transport prior to condensation on the substrate.

In the preferred embodiment of the invention, after deposition of the silver coating, stripes of nickel are deposited in deposition chamber 26, by e-beam evaporation, at a thickness of 12 to 20 nanometers. A water-cooled mask 44 prevents deposition in selected areas, thereby resulting in a striped nickel coating.

After deposition of the nickel stripes, the exposed portions of the silver layer are subjected to a bleaching agent, such as, for example, a solution of potassium chloride and potassium chromate (not shown). Bleaching as used herein and in the claims is a technique used to convert a portion of the silver layer to a silver halide, such as AgCl. The bleaching step is used to convert approximately 25-40 percent of the thickness of the silver layer in the exposed areas to silver chloride, as indicated by 8 in Fig. 2. The percentage of the thickness of AgCl converted depends upon the desired end use of the ISE. For example, for chloride ISEs, 36 percent of the thickness is converted, and for sodium ISEs, 26 percent of the thickness of the Ag layer is converted to AgCl. The areas of the silver layer under the nickel coated stripes remain essentially unchanged.

When prepared in accordance with the present invention, the composite Ag/Ni coatings of the present invention exhibit no vertical cracking of the AgCl layer during bleaching, even though no aging of the Ag is required prior to Ni stripe deposition, and even though no adhesion promoting layer is applied to the PET substrate. Consequently, the composite ISE of the present invention can be produced using less materials and in less manufacturing operations (no aging of Ag step). Perhaps more importantly, the present invention alleviates the need for an inventory system, storage facility, and so forth, needed to facilitate aging of the silver layer.

The PET/Ag/AgCl/Ni composite thus formed is operable as a chloride ion selective electrode. A protective overcoat may be selectively coated over the composite device. For example, cellulose acetate may be applied over the AgCl portion in a chloride ion sensitive electrode.

To produce other ion sensitive electrodes (such as potassium or sodium ISEs) using the PET/Ag/AgCl/Ni composite of the present invention, a further step may be conducted in which areas of the silver chloride are selectively overcoated with an electrolyte containing gel and an ion selective membrane, such as, for example, is indicated by 10 and 11, respectively, in Fig. 1. Conventional ion selective membranes are materials which incorporate hydrophobic polymers in combination with an ionophoric (facilitates ion transport) material. Examples of electrolyte containing gels are NaCl containing

gels (for Na ISE's) and KCl containing gels (for K ISE's). Examples of such ion selective membranes are those that contain valinomycin (for K ISE's) and methyl monensin (for Na ISE's). For further explanation see U.S. Patent No. 4,214,968. Electrodes produced in connection with the present invention perform as well as electrodes prepared in accordance with prior art methods, even though no adhesion layer was included on the PET substrate, and there was no aging of the silver layer prior to nickel deposition.

The invention may be more easily comprehended by reference to specific examples. It must be understood, however, that these examples are provided only for purposes of illustration, and that the invention may be practiced otherwise than as specifically illustrated without departing from its spirit and scope.

Example 1

A vacuum web coating apparatus 20 similar to that illustrated in Fig. 2 was evacuated to a base pressure of about 5.3×10^{-4} Pascals. A roll of approximately 175 nm thick poly(ethylene terephthalate) (PET) film substrate (having no adhesion promoting sublayer thereon) was unrolled and transported through the coater, traveling first through a glow discharge chamber 22 where it was subjected to a glow discharge pretreatment. The atmosphere during the glow discharge pretreatment step was 100 percent nitrogen. The nitrogen gas was bled into chamber 22 at a pressure of 6.65 Pascals. The glow discharge cathode was then activated at a power chosen to give a treatment energy of 1.5 joules/cm² (as calculated from $E = W \cdot t / A$, where $W = 90$ watts total cathode power, $A = 329$ cm² cathode area, and $t = 5.4$ seconds exposure time of a given area of the support to the glow discharge).

After the glow discharge treatment, the PET support was transported to deposition chambers 24 and 26, each of which were set up to deposit silver (thus no mask 44 was employed). A layer of metallic silver approximately 700 nm thick or 7.35 g/m² was deposited by electron-beam gun vacuum evaporation of a silver metal contained in crucible 25.

Within 8 hours the silver film above coated was overcoated with a series of parallel nickel stripes, approximately 8.4 mm wide and 12 nm thick, separated by 23.4 mm wide uncoated spaces. The nickel layer 8 was also applied by electron-beam gun evaporation from a nickel source in a vacuum web coater using standard technique as described above.

The Ni coated film was then treated with an aqueous solution of 8.45 g/l potassium chlorochromate as described in US Pat. No. 4,214,968, Example 2. This process converted approximately 36 percent of the thickness of the silver layer in the non-Ni-striped areas to silver chloride as indicated by 8 in Fig. 1. The areas of the silver layer under the nickel coated stripes remained essentially unchanged.

Surface examination of the electrode samples with a low power 50X reflecting microscope revealed absolutely no cracking in the silver-silver chloride layer.

The resulting composite ISE gave excellent response, that is, essentially equal to controls prepared using prior art processes of manufacture.

A 'tape test' was used to evaluate adhesion of the layers. A piece of cellulose adhesive tape was applied to the top electrode surface using finger pressure, then quickly pulled off. Tests with repeated samples of this electrode showed no separation of layers and the electrode structure invariably remained intact.

Comparative Example 1:

This example, which illustrates the prior method of manufacture, is virtually the same as Example 1, only the PET substrate had an adhesion promoting sublayer applied thereon. A 175 nm thick PET film having an adhesion promoting sublayer thereon of poly(acrylonitrile-co-vinylidene chloride-co-acrylic acid) was used as the substrate. After being coated with a 700 nm thick silver layer, metallic nickel stripes approximately 12 nm thick were deposited within a period of 8 hours. The composite material was then subjected to the same bleaching process described in Example 1. Examination of the surface of the material with a low power (50X) reflecting microscope after bleaching revealed extensive cracking of the silver-silver chloride layer in between the nickel metal stripes. The cracks were oriented essentially perpendicular to the nickel stripes and the substrate and continued through to the base.

Although nickel stripes are preferred in the electrodes of the invention, in the ISEs described above other conductive metals, such as, for example, Ti, alloys of conductive metals, and so forth, can be substituted for the nickel stripes. Further, an operable ISE can be configured without any conductive metal stripes. Thus, for example, the present invention can be utilized to manufacture an ISE comprising a AgCl layer over a Ag metal layer on a plastic substrate, with no conductive metal stripes thereon, such as is disclosed in U.S. Patent No. 4,214,968.

Other embodiments of the invention include

an ion selective electrode, comprising:
a polymeric substrate having a major surface whose composition contains nitrogen; and
a layer of a silver containing material deposited directly on said polymeric substrate, selected areas of said silver layer comprising a silver halide, the remainder of said silver layer comprising silver metal areas.

The ion selective electrode may further comprise a layer of conductive metal e.g. nickel selectively deposited over said silver metal areas.

The electrode may further comprise a layer of an

electrolyte containing material selectively deposited over said silver halide; and

a layer of an ion selective material deposited over said electrolyte containing material.

The electrode may further comprise a layer of an ion selective material selectively deposited over said silver halide.

The electrode may further comprise a layer of protective material over said silver halide areas.

The polymeric substrate may be poly(ethylene terephthalate).

Claims

1. A method of preparing an ion-selective electrode element comprising:

(a) subjecting at least one surface of a polymeric substrate, having no adhesion-promoting subcoating thereon, to a glow discharge plasma in an essentially oxygen-free atmosphere containing nitrogen, the pressure of the atmosphere being from 1 to 67 pascals, such that the treatment energy is between 1.1 and 4 joules/cm²;

(b) depositing a layer of silver on said at least one treated surface;

(c) depositing nickel on selected areas of said silver layer; and

(d) exposing uncoated areas of said silver layer to a bleach bath to convert at least a portion of said silver layer to a silver halide.

2. The method of claim 1, wherein said nickel deposition step (c) is carried out within 8 hours of said silver deposition step (b).

3. The method of claim 1 or claim 2, further comprising the steps of:

(e) applying an electrolyte-containing material to said uncoated areas of said silver-containing layer; and

(f) applying an ion-selective material to said electrolyte-containing material.

4. The method of any one of claims 1 to 3, further comprising the step of:

(g) covering the uncoated areas of said silver-containing layer with a protective material.

5. The method of any one of claims 1 to 4, wherein said atmosphere comprises 2% nitrogen and 98%

argon.

6. An electrochemical analysis element comprising:

(1) a polymeric substrate having no adhesion-promoting subcoating thereon and having a major surface containing nitrogen;

(2) a layer of silver deposited directly on said major surface, the silver layer being covalently bonded to said major surface by amine, imine or amide bonds; and

(3) a layer of nickel deposited on selected areas of said silver layer;

wherein uncoated areas of said silver layer comprise at least in part silver halide.

7. The element of claim 6, further comprising:

(4) a layer of an electrolyte-containing material on uncoated areas of said silver-containing layer; and

(5) a layer of an ion-selective material on said electrolyte-containing material.

8. The element of claim 6 or claim 7, further comprising:

(6) a protective layer on uncoated areas of said silver-containing layer.

9. The method of claim 4, wherein said protective material or layer is of cellulose acetate.

10. The method of any one of claims 1 to 5, wherein the polymeric substrate is of poly(ethyleneterephthalate).

11. The element of claim 8, wherein said protective material or layer is of cellulose acetate.

12. The element of any one of claims 6 to 9, wherein the polymeric substrate is of poly(ethyleneterephthalate).

Patentansprüche

1. Verfahren zur Herstellung eines ionenselektiven Elektrodenelements, umfassend folgende Stufen:

(a) mindestens eine Oberfläche eines polymeren Substrats, das mit keiner haftungsfördernden Unterschicht versehen ist, wird in einer im wesentlichen sauerstofffreien Atmosphäre, die Stickstoff enthält, einem Glimmentladungs-

- plasma ausgesetzt, wobei der Druck der Atmosphäre 1 bis 67 Pascal beträgt, so daß die Behandlungsenergie 1,1 bis 4 Joules/cm² beträgt;
- (b) eine Silberschicht wird auf der mindestens einen behandelten Oberfläche abgeschieden;
- (c) Nickel wird auf ausgewählten Bereichen der Silberschicht abgeschieden; und
- (d) unbeschichtete Bereiche der Silberschicht werden einem Bleichbad ausgesetzt, um mindestens einen Teil der Silberschicht in Silberhalogenid überzuführen.
2. Verfahren nach Anspruch 1, wobei die Nickelabscheidungsstufe (c) innerhalb von 8 Stunden nach der Silberabscheidungsstufe (b) durchgeführt wird.
3. Verfahren nach Anspruch 1 oder 2, ferner umfassend folgende Stufen:
- (e) ein elektrolythaltiges Material wird auf die unbeschichteten Bereiche der silberhaltigen Schicht aufgebracht; und
- (f) ein ionenselektives Material wird auf das elektrolythaltige Material aufgebracht.
4. Verfahren nach einem der Ansprüche 1 bis 3, ferner umfassend folgende Stufe:
- (g) die unbeschichteten Bereiche der silberhaltigen Schicht werden mit einem Schutzmaterial bedeckt.
5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Atmosphäre 2% Stickstoff und 98% Argon umfaßt.
6. Elektrochemisches Analyseelement, umfassend:
- (1) ein polymeres Substrat, das keine haftungsfördernde Unterschicht aufweist und eine Stickstoff enthaltende Hauptoberfläche aufweist;
- (2) eine direkt auf der Hauptoberfläche abgeschiedene Silberschicht, wobei das Silber kovalent über Amin-, Imin- oder Amidbindungen an die Hauptoberfläche gebunden ist; und
- (3) eine auf ausgewählten Bereichen der Silberschicht abgeschiedene Nickelschicht;
- wobei unbeschichtete Bereiche der Silberschicht mindestens teilweise Silberhalogenid umfassen.
7. Element nach Anspruch 6, ferner umfassend:
- (4) eine Schicht eines elektrolythaltigen Materials auf unbeschichteten Bereichen der silberhaltigen Schicht; und
- (5) eine Schicht eines ionenselektiven Materials auf dem elektrolythaltigen Material.
8. Element nach Anspruch 6 oder 7, ferner umfassend:
- (6) eine Schutzschicht auf unbeschichteten Bereichen der silberhaltigen Schicht.
9. Verfahren nach Anspruch 4, wobei das Schutzmaterial oder die Schutzschicht aus Celluloseacetat besteht.
10. Verfahren nach einem der Ansprüche 1 bis 5, wobei das polymere Substrat aus Poly-(ethylenterephthalat) besteht.
11. Element nach Anspruch 8, wobei das Schutzmaterial oder die Schutzschicht aus Celluloseacetat besteht.
12. Element nach einem der Ansprüche 6 bis 9, wobei das polymere Substrat aus Poly-(ethylenterephthalat) besteht.

Revendications

1. Procédé de préparation d'un élément d'une électrode sélective d'ions consistant :

(a) à soumettre au moins une surface d'un substrat polymérique non recouvert d'une sous-couche favorisant l'adhérence, à un plasma de décharge lumineuse dans une atmosphère essentiellement exempte en d'oxygène et contenant de l'azote, la pression de l'atmosphère étant comprise entre 1 et 67 Pa, de façon telle que l'énergie de traitement est comprise entre 1,1 et 4 joules/cm² ;

(b) à appliquer une couche d'argent sur au moins une desdites surfaces traitées ;

(c) à appliquer du nickel sur des surfaces sélectionnées de ladite couche d'argent ; et

(d) à exposer des surfaces non recouvertes de ladite couche d'argent à un bain de blanchiment pour transformer au moins une partie de ladite couche d'argent en un halogénure d'argent.

2. Procédé selon la revendication 1, dans lequel ladite phase (c) d'application de nickel est effectuée dans un laps de temps de 8 heures après ladite phase (b) d'application d'argent.

3. Procédé selon la revendication 1 ou 2, comprenant en outre les phases consistant :

(e) à appliquer un matériau contenant un électrolyte sur lesdites surfaces non recouvertes de ladite couche contenant de l'argent ; et

(f) à appliquer un matériau sélectif d'ions sur

ledit matériau contenant un électrolyte.

6 à 9, dans lequel le substrat polymérique est du polyéthylène téréphthalate.

4. Procédé selon l'une quelconque des revendications 1 à 3, comprenant en outre la phase consistant :
 (g) à recouvrir les surfaces non recouvertes de ladite couche contenant de l'argent, avec un matériau de protection. 5
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel ladite atmosphère se compose de 2 % d'azote et de 98 % d'argon. 10
6. Élément d'analyse électrochimique comprenant :
 (1) un substrat polymérique non recouvert d'une sous-couche favorisant l'adhérence et ayant une surface principale contenant de l'azote ; 15
 (2) une couche d'argent appliquée directement sur ladite surface principale la couche d'argent étant liée de façon covalente à ladite surface principale par des liaisons d'amines, d'imines ou d'amides ; et 20
 (3) une couche de nickel appliquée sur des surfaces sélectionnées de ladite couche d'argent ; 25
 où des surfaces non recouvertes de ladite couche d'argent se composent au moins en partie d'halogénure d'argent. 30
7. Élément selon la revendication 6, comprenant en outre :
 (4) une couche d'un matériau contenant un électrolyte sur des surfaces non recouvertes de ladite couche contenant de l'argent ; et 35
 (5) une couche d'un matériau sélectif d'ions sur ledit matériau contenant un électrolyte.
8. Élément selon la revendication 6 ou 7, comprenant en outre :
 (6) une couche de protection sur des surfaces non recouvertes de ladite couche contenant de l'argent. 45
9. Procédé selon la revendication 4, dans lequel ledit matériau ou ladite couche de protection est de l'acétate de cellulose.
10. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le substrat polymérique est du polyéthylène téréphthalate. 50
11. Élément selon la revendication 8, dans lequel ledit matériau ou ladite couche de protection est de l'acétate de cellulose. 55
12. Élément selon l'une quelconque des revendications

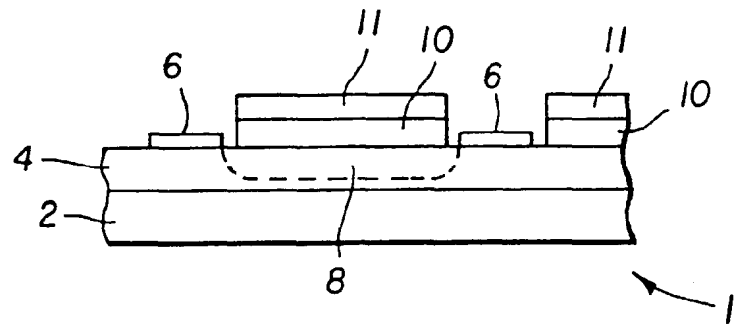


FIG. 1

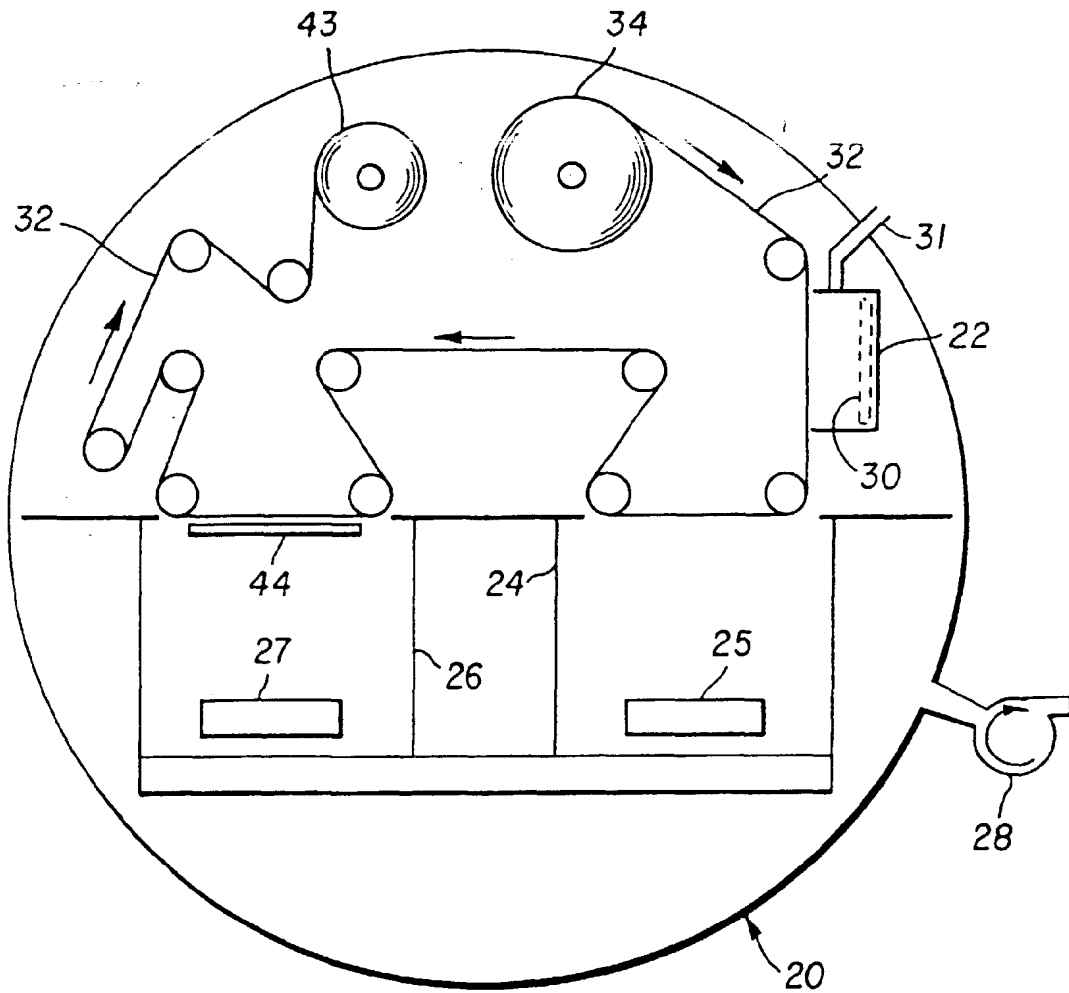


FIG. 2